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A New Method for Growth and Analysis of Next-generation Infrared (IR) Detector Materials

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ARL-TR-4739 **March 2009**

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REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
March 2009	Final	

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
A New Method for Growth and Analysis of Next-generation Infrared (IR) Detector Materials	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
John D. Demaree and Stefan Svensson	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-MA Aberdeen Proving Ground, MD 21005-5069	ARL-TR-4739

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report describes the development of a new analysis and crystal growth method for next generation infrared materials, namely, dilute nitride III-V semiconductors, which may be used in future low-cost night vision systems. The key to this method is isotopic enrichment of nitrogen-15 during material growth via molecular beam epitaxy, which allows enhanced detection of nitrogen using resonant nuclear reaction analysis. We synthesized films of gallium arsenide nitride (GaAsN) using nitrogen gas enriched in nitrogen-15 and examined them using x-ray diffraction, secondary ion mass spectroscopy, and nuclear reaction analysis. This analysis confirmed that the incorporation of nitrogen-15 into the material corresponds with the expected enrichment of the feed gas. This finding opens up the possibility of examining the material using ion beam channeling methods to ascertain the lattice position of the incorporated nitrogen atoms.

15. SUBJECT TERMS

Infrared detector, gallium arsenide, MBE, nuclear reaction

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			John D. Demaree
U	U	U	UU	20	19b. TELEPHONE NUMBER (*Include area code*) (410) 306-0840

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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Acknowledgments

This research was supported by the U.S. Army Research Laboratory's (ARL) Director's Research Initiative (DRI) and the Missile Defense Agency. We would like to thank Mark Wood for the secondary ion mass spectrometry (SIMS) measurements.

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1. Objective

The Army's need for night-vision superiority is well known. To meet this need, the Army requires infrared (IR) detector materials with high detectivity that can be manufactured at low cost. Mercury cadmium telluride (MCT) is the current material technology of choice for performance reasons, but it is a II-VI material that has few other applications, can only be processed in dedicated fabrication facilities, and is, therefore, very costly. In contrast, III-V materials have many commercial and military applications, so an IR materials technology that can piggyback on the existing industrial III-V infrastructure would realize a significant cost savings. Until recently there has not been a suitable III-V-based alternative to MCT, since the common III-V compounds cannot absorb in the long-wavelength band (8–12 μm) with the high quantum efficiency associated with direct bandgap materials like MCT. If one can develop a III-V direct bandgap material without intrinsic interfaces (as found in, e.g., a Quantum Well Infrared Photodetector (QWIP) or type II strained layer superlattices), we may realize the detectivity and durability needed for low-cost, high performance night vision systems.

It has been theoretically predicted that the novel materials class labeled dilute-nitrides, specifically the compound gallium indium antimonide nitride (GaInSbN), can be lattice matched to gallium antimonide (GaSb) to produce a direct band-gap material that can detect out to 20 μm, thus covering most tactical and strategic applications (*1*). Such materials would require the substitutional incorporation of 4–5% nitrogen (N) into the group V sites of the semiconductor lattice. Until recently the highest concentration of nitrogen reported in $GaSb_{1-x}N_x$ was 1.75% (*2*). Recent work at the U.S. Army Research Laboratory (ARL) has doubled this to 3.5%, and there is no indication that a limit has been reached. However, at present, the optical quality of as-grown material is usually reduced, presumably because much of the nitrogen is incorporated at undesirable locations in the crystal lattice. In order to successfully further develop these materials, one must quantify both the concentration and location of the nitrogen atoms in the lattice.

2. Approach

2.1 Background

At ARL, we are developing a new crystal growth and analysis method, which combines two previously unrelated capabilities at two of ARL's research directorates, the Weapons and Materials Research Directorate (WMRD) and the Sensors and Electron Devices Directorate (SEDD). In previous work, researchers at WMRD showed that firing-induced nitrogen incorporation in gun barrel steel can have the beneficial effect of reducing the erosion of the

barrel (*3*). A critical part of that project involved measuring the depth distribution of nitrogen under the surface of gun steels, using an ion beam analysis technique known as resonant nuclear reaction analysis (RNRA). In this method, a positive ion accelerator is used to direct a beam of light energetic ions onto a target material. A very small fraction of the incident ions will approach an atomic nucleus in the target material so directly that the strong nuclear forces that bind nuclei together can overcome the electromagnetic repulsion of the positively charged ions and nuclei, and the two merge into a single, heavier atomic nucleus. Such "compound nuclei" are formed in highly excited states and release that energy by either breaking apart into energetic particles, releasing high-energy gamma rays, or both. For example, when a proton beam is directed onto a sample containing nitrogen, some protons and nuclei of a particular nitrogen isotope (^{15}N) combine to form excited ^{16}O nuclei, which almost immediately split apart (into ^{12}C and alpha particles), releasing a 4.43 MeV gamma ray. This characteristic gamma ray is a "fingerprint" for the presence of ^{15}N in the sample.

Under ordinary circumstances, the sensitivity of RNRA is limited by the natural abundance of the ^{15}N isotope, which is only 0.366% of natural nitrogen. When natural isotopic abundances of nitrogen are present, as in the case of gun barrel surface reactions, the uncertainty in the measurement (and the minimum detectable amount) is on the order of 0.3 atomic percent. In this work, molecular beam epitaxy (MBE) is employed to grow gallium arsenide nitride (GaAsN) films using isotopically enriched ^{15}N gas. Enriched nitrogen is commercially available in concentrations approaching 100% of the ^{15}N isotope, which means that the sensitivity of the RNRA measurements should be improved by more than two orders of magnitude over previous studies.

2.2 Experimental Procedure

Thin films of GaAsN were grown on gallium arsenide (GaAs) substrates by MBE, using a system equipped with a commercial nitrogen gas injector, which includes a unit that can form a plasma that produces energetic, single nitrogen atoms (nitrogen is otherwise always found in its diatomic N_2 state). The injector is fed gaseous nitrogen from one of two pressurized bottles containing either natural nitrogen gas (primarily ^{14}N) or nitrogen gas that has been enriched with the ^{15}N isotope.

The film growth started with the desorption of the oxide from the GaAs substrate surface by heating the sample wafer in an arsenic (As) flux to a specific temperature at which a regular reflection high-energy electron diffraction (RHEED) pattern is observed. We then lowered the sample temperature to a value suitable for growth of GaAs, and deposited a 250-nm "buffer layer" of GaAs to produce material that was cleaner and had a smoother surface than the original substrate. Subsequently, we lowered the temperature to a value that is suitable for growth of GaAsN and pressurized the gas delivery line with enriched nitrogen gas. Radio frequency (RF) power was supplied to the plasma source and the mass flow controller (MFC) was set to a relatively large value that increased the background pressure in the reactor to near 1E-5 Torr.

When the plasma struck (visible light was observed), we immediately reduced the MFC setting to a value known to produce a stable reactor pressure. The system pressure and the plasma source were allowed to stabilize over a 40-min wait period, after which the sample was exposed to molecular beams of gallium (Ga) and As until a film approximately 200 nm thick was deposited. We repeated this procedure using both the naturally abundant nitrogen gas and the isotopically enriched nitrogen gas.

Finally, we examined the grown films of GaAsN and GaAs^{15}N using secondary ion mass spectrometry (SIMS), x-ray diffraction, and RNRA. RNRA measurements were made using a 900 keV proton beam from a National Electrostatics 5SDH-2 positive ion accelerator. We measured the characteristic gamma rays from the (p,^{15}N) reaction using a bismuth germanate scintillation detector.

3. Results

The successful incorporation of nitrogen into the growing GaAs film (i.e., GaAsN) was determined by recording an x-ray diffraction rocking curve, as exemplified in figure 1. The main peak at zero is a result of diffraction from the GaAs substrate, and the smaller peak at ~2100 arc sec is evidence of the GaAs^{15}N film grown using isotopically enriched ^{15}N gas. The many smaller peaks in between are Pendelloesung fringes, whose presence indicates flatness of the film. Their frequency can furthermore be used to determine the thickness of the layer. The red curve is the theoretically predicted signal from a GaAsN film given a film thickness of 193 nm and a nitrogen content of 3.9% of the group V sites. The overall excellent agreement between the experimental (black) and theoretically predicted (red) curves is evidence for a very high-quality sample, equivalent to the crystalline quality of the GaAsN films that have grown using naturally abundant nitrogen gas. The use of enriched gas had no apparent effect on the growth or quality of the resulting material.

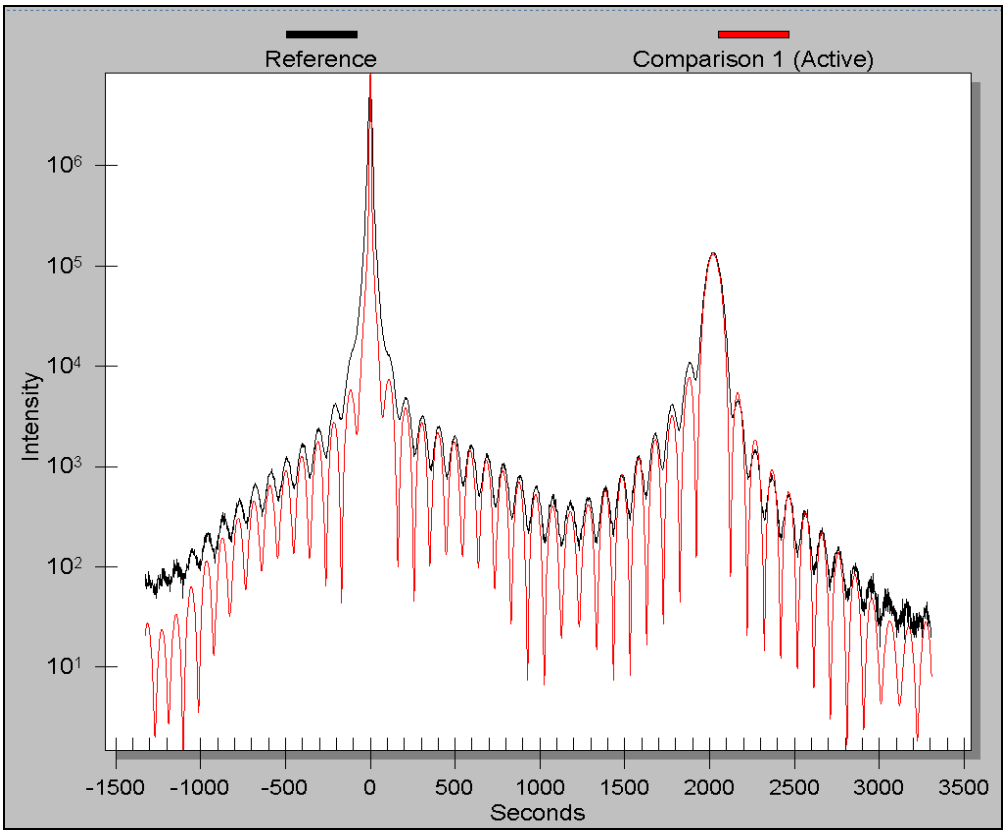

Figure 1. An x-ray rocking curve from a $GaAs_{1-x}{}^{15}N_x$ film (x=3.87%); the pronounced Pendelloesung fringes and overall good agreement between experiment (black) and theory (red) indicate excellent crystalline quality.

To verify the incorporation of ^{15}N in the $GaAs^{15}N$ films, we performed SIMS on the same sample and a reference sample, which had been grown with natural nitrogen in an otherwise identical way (figure 2). Note that because of the detectability limits of SIMS, the secondary ions actually measured are complexes of Ga and N, with total masses of 83 and 84 amu. The ratio of the intensity of these two signals yields the $^{15}N/^{14}N$ ratio in the materials. In the GaAsN grown with natural nitrogen gas, SIMS yielded a $^{15}N/^{14}N$ ratio of 0.0037—exactly as expected from natural nitrogen abundance. In the case of the film grown with enriched gas, this ratio was measured as ~55, corresponding roughly to the expected enrichment of ^{15}N cited by the gas supplier (~98%).

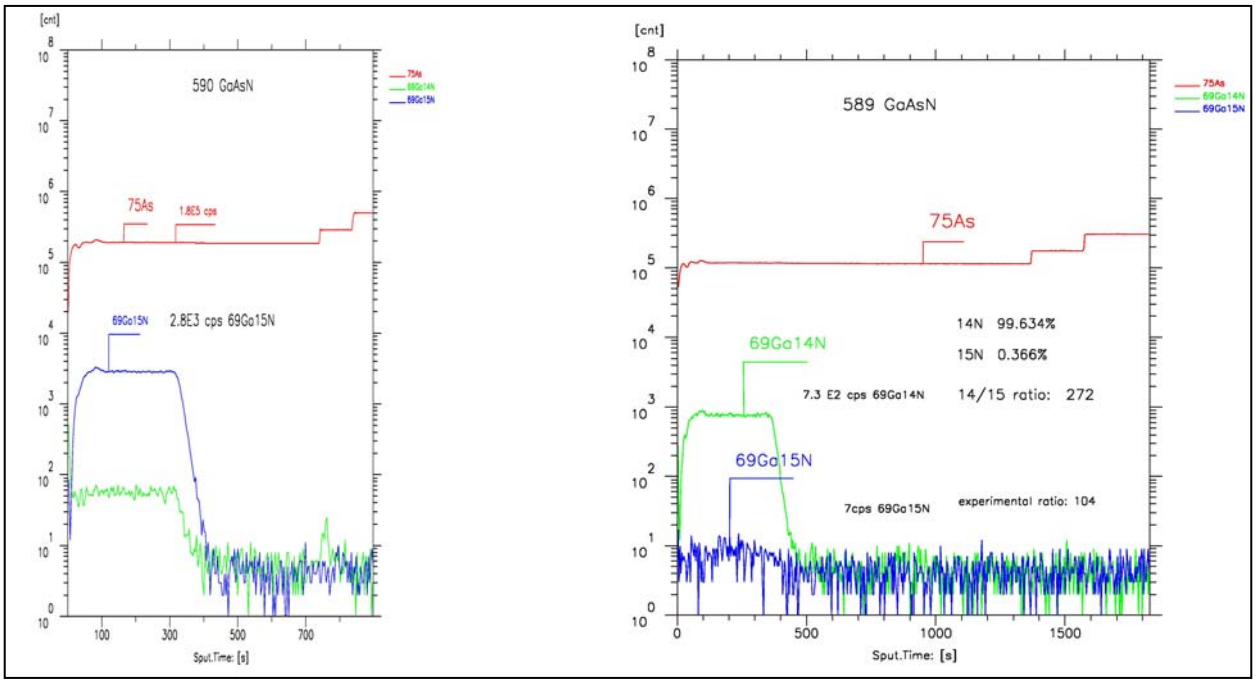

Figure 2. SIMS profiles of GaAsN films grown with enriched ^{15}N gas (left) and naturally abundant nitrogen gas (right).

The incorporation of the ^{15}N isotope into the films was also confirmed using RNRA, as shown in figure 3. The energy of the incident proton beam was adjusted to 900 keV so that protons would slow to the resonant reaction energy (897 keV) just beneath the surface of the material. At that energy, protons and ^{15}N nuclei form a compound nucleus (^{16}O) in a highly excited state, which almost immediately decays via the emission of an alpha particle into an excited ^{12}C nucleus. This excited ^{12}C transitions to its ground state via the emission of a gamma ray with an energy of 4.43 MeV. In figure 3, this peak, and its associated first escape peak, is evident at 4.43 MeV and 3.92 MeV. The intensity of these peaks over the natural radioactivity background (cosmic rays and the thallium-208 gamma at 2.62 MeV) can be related to the actual concentration of ^{15}N in the film, and studies are currently underway to quantify these results.

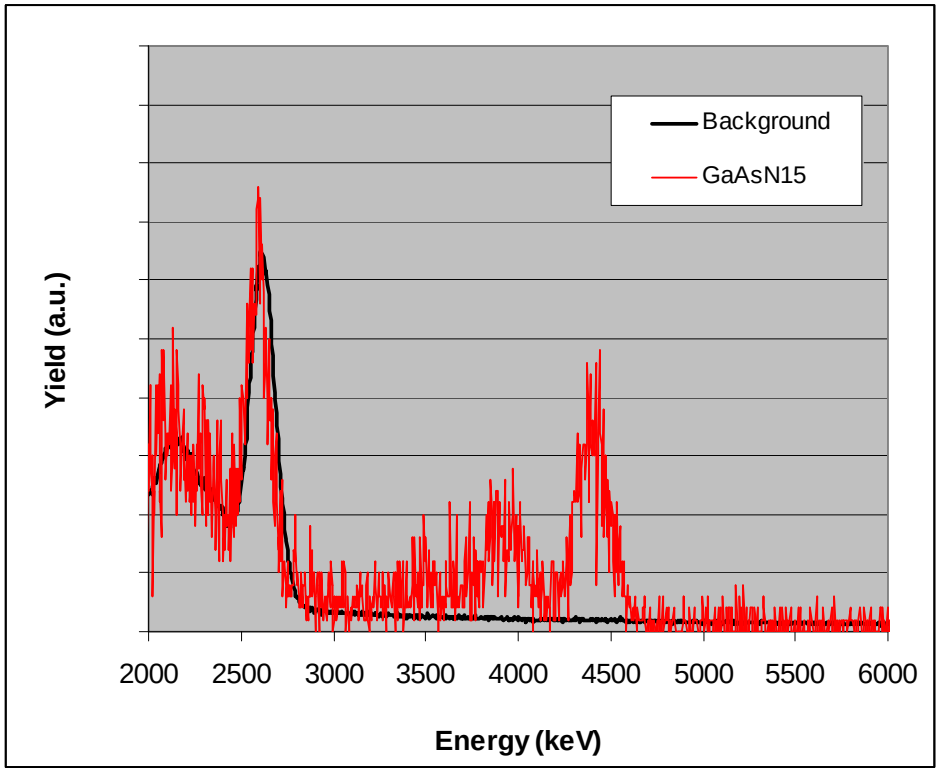

Figure 3. Gamma ray spectrum obtained using 900 keV protons incident on 200-nm thick GaAs^{15}N.

In more recent studies, we have begun to investigate the actual structure of the GaAsN films using a combination of RNRA and "ion beam channeling" techniques. In these measurements, currently underway, the single-crystal target is aligned with the incident proton beam using a precision goniometer and gamma ray yields are measured as the sample is brought in and out of alignment. If the incorporated nitrogen occupies substitutional sites in the III-V crystal structure—as desired for optimal effect on the bandgap of the material—the aligned planes and axes of the material will block the proton beam from interaction with the ^{15}N nuclei when the sample is perfectly aligned, resulting in a large reduction in gamma ray yield. If, however, the nitrogen atoms are merely occupying interstitial sites in the lattice, contributing only unwanted optical scattering and decreased photoluminescence, then this alignment procedure will not result in such a large decrease in gamma ray yield (*4*). Identification of the actual lattice position of the incorporated nitrogen is a key factor in the development of these materials and will guide MBE growth parameters, post-deposition treatments, and eventual optimization of these IR detector materials.

4. Conclusions

In this effort, we have demonstrated the growth of dilute nitride semiconductors using isotopically enriched nitrogen gas in GaAsN using MBE. The crystalline quality of the films was high and was not affected by the use of enriched gas. We confirmed the incorporation of ^{15}N into the grown material using SIMS and RNRA. The isotopic enrichment in the semiconductor material results in high gamma ray yields and will allow the future optimization of dilute nitrides using RNRA and ion beam channeling.

5. References

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6. Transitions

The successful completion of this fiscal year 2008 (FY08) Director's Research Initiative (DRI)—the demonstration of the growth of a dilute-nitride semiconductor using isotopically enriched nitrogen and the detection of that nitrogen using nuclear reaction analysis—is an enabling technology for more rapid detection of the position of that nitrogen in the semiconductor lattice. Measuring the nuclear reaction rate while precisely aligning the sample with the ion beam (so-called "ion beam channeling") will allow us to assess the fraction of nitrogen on beneficial substitutional lattice sites versus property-degrading interstitial sites, and more rapidly optimize the growth and processing parameters needed to produce an efficient IR detector material. The results of this FY08 DRI are therefore being transitioned into both a follow-on FY09 DRI project, in which this nuclear measurement will be demonstrated, and a program funded by the Missile Defense Agency, in which processing parameters will be modified to optimize material performance.

Acronyms

ARL	U.S. Army Research Laboratory
As	arsenic
DRI	Director's Research Initiative
FY08	fiscal year 2008
Ga	gallium
GaAs	gallium arsenide
GaAsN	gallium arsenide nitride
GaInSbN	gallium indium antimonide nitride
GaSb	gallium antimonide
IR	infrared
MBE	molecular beam epitaxy
MCT	mercury cadmium telluride
MFC	mass flow controller
N	nitrogen
QUIP	Quantum Well Infrared Photodetector
RF	radio frequency
RHEED	reflection high-energy electron diffraction
RNRA	resonant nuclear reaction analysis
SEDD	Sensors and Electron Devices Directorate
SIMS	secondary ion mass spectrometry
WMRD	Weapons and Materials Research Directorate

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